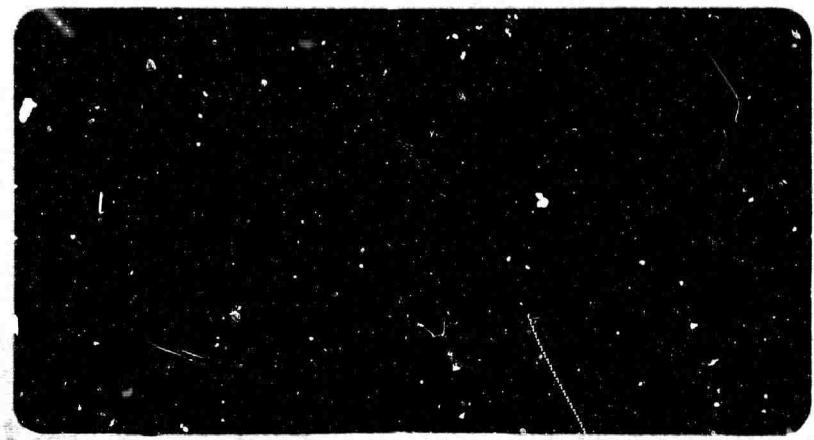


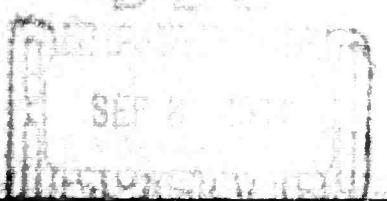
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HIGH ENERGY OXIDIZERS

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Project NR 093-035

Richmond Research Center
Richmond, California

STAUFFER CHEMICAL COMPANY
Richmond Research Center
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

ARPA No. 399-62

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

Quarterly Technical Summary Report
for the Period May 1, 1964 to August 1, 1964

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of December 1963.

Summary

The preparation of ClF_2ClO_4 , ClF_2ClO_3 , ClF_2NO_3 , ClF_2NO_2 , ClF_2NO and of similar Cl, F, N, O containing compounds is being investigated. Some evidence was obtained for the existence of ClF_2NO or $\text{ClF}\cdot\text{NOF}$, but it was shown to have a lower thermal stability than the $\text{ClF}_3\cdot\text{NOF}$ complex.

Abstract

This is the second Quarterly Technical Summary Report of our second year's investigation of complexes based on chlorinetrifluoride.

The reaction of nitrogen pentoxide and chlorinetrifluoride did not result in the desired $\text{ClF}_2\text{NO}_3^-$. The main product isolated was nitrylfluoride. The small amount of residue obtained did not contain chlorine in any valency state.

When chlorinetrifluoride reacted with fuming nitric acid again no $\text{ClF}_2\text{NO}_3^-$ could be detected. A solid residue of low thermal stability was obtained, which also did not contain any chlorine. In the vapor phase the presence of ClO_2F was established.

The reaction between NOF and ClF gave a solid complex at $-78^\circ\text{C}.$, which rapidly decomposed at slightly higher temperatures. No complex formation was observed between ClO_3F and ClF in the range of $-78^\circ\text{C}.$ to room temperature.

Introduction

Our earlier studies on the reaction of nitrates and perchlorates with chlorinetrifluoride did not show the formation of the expected difluorochlorinium salts. With AgNO_3 , the products were NO_2F and AgF_2 , with KClO_4 no reaction took place. Investigations were continued to obtain ionic compounds containing both anions and cations of high energy. For this purpose, the reactions of chlorinefluorides with N_2O_5 , HNO_3 , NOF and ClO_3F were studied.

Discussion

Reaction between chlorinetrifluoride and N_2O_5

The following reaction was desired:



The reactants were condensed together at -196°C . Upon warming up a vigorous reaction took place as soon as the chlorinetrifluoride melted. The volatile products, analyzed by IR spectroscopy, consisted of NO_2F and excess ClF_3 , but no chlorinemonofluoride was detected.

A small amount of solid residue was obtained, which was stable up to room temperature, although it slowly deliberaed nitrous vapors. The analysis showed high fluorine and nitrogen, but no chlorine content. The absence of the difluorochlorinium cation was also indicated by its mild reaction with water in which it was clearly soluble. Analysis excludes the possibility of hexafluorosilicate salt. It could be a complex between HF and nitrogenoxides or nitrogenoxyfluorides. Its composition is under further study.

Reaction between chlorinetrifluoride and nitric acid

The fluorination of nitric acid with elementary fluorine gives fluorinenitrate according to the following equation(1):



If the fluorination of HNO_3 is carried out with chlorinetrifluoride, the formation of $\text{ClF}_2^+\text{NO}_3^-$ might be expected:

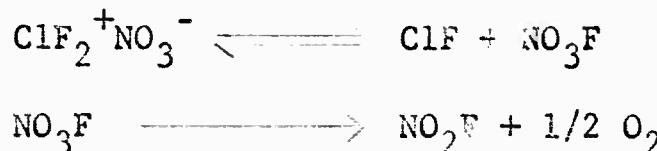


The reactants were brought together gradually at -78°C ., where a vigorous reaction took place. The volatile part of the reaction mixture contained SiF_4 , ClO_2F , ClF_3 , HNO_3 , N_2O_4 and NO_2 . A white

(1) Cady, G. H., J. Am. Chem. Soc. 56, 2635 (1934)

solid material was left after the evaporation of the volatile part, which melted at around -10°C . In molten state it reacted rapidly with the quartz container under the formation of SiF_4 . The liquid residue consisted of nitric acids and nitrogen oxides.

In the reaction of chlorinetrifluoride with AgNO_3 , HNO_3 and N_2O_5 , nitrylfluoride was obtained as main product. This might be explained by the following two equations:



The second reaction was investigated by Cady and found to be catalyzed by fluorine and nitrogen oxides⁽²⁾. By the continuous decomposition of NO_3F the first equilibrium could be shifted completely to the right.

Complex formation of chlorinemonofluoride

Difluorochlorinium cation containing compounds were prepared in the past from chlorinetrifluoride by the abstraction of a fluorine anion. Theoretically they could be prepared from chlorinemonofluoride according to the following reaction equation:



The actual reaction mechanism can involve the formation of an intermediate complex without the formation of a fluorine cation, which would require a high activation energy.

Reactions between ClF_3 and FX such as NOF are known. In these cases, however, the chlorinetrifluoride acts as Lewis acid



The reaction of NOF with chlorinemonofluoride in CFCl_3 as a solvent was found to give a solid complex at -78°C ., but it decomposed rapidly at slightly higher temperatures. During the decomposition a blue color developed, indicating the presence of nitrogen oxygen radicals.

In the complex formation between NOF and ClF, the existence of either NOF_2^- or ClF_2^- might be expected. So far both anions are unknown.

Under similar conditions no interaction was observed between ClO_3F and chlorinemonofluoride.

(2) Cady G. H., Skjens, W. E., J. Am. Chem. Soc. 80, 5640 (1958)

Experimental

Starting materials

Chlorinetrifluoride was purified as described in earlier reports. Perchlorylfluoride was obtained from Pennsalt Chem. Co., while ClF and NOF came from Ozark-Mahoning Co. They were used without further purification. Red fuming nitric acid (B&A) was purged slowly with oxygen until it turned to yellow. Nitrogenpentoxide was prepared from nitric acid and phosphorus pentoxide. The product was purified by fractional sublimation. Trichlorofluoromethane was obtained from Matheson Co.

Reaction of nitrogenpentoxide with chlorinetrifluoride

Five grams of nitrogenpentoxide was sublimed into a trap in the vacuum line and an excess of chlorinetrifluoride (appr. 15 ml.) was condensed into the trap at -196°C . The trap was warmed up very cautiously and upon the melting of the chlorinetrifluoride a vigorous reaction took place. A homogeneous dark brown solution formed. The reaction products were condensed at -196°C . in another trap and fractionated. The fractions were identified by their IR gas spectra using a 10 cm long cell with AgCl windows. Beside ClF_3 nitryl fluoride was found to be the main product. When the reaction was carried out with less pure nitrogenpentoxide, ClO_2F , NO_2 , N_2O_4 , HNO_3 and an unidentified compound with absorption at 1745 and 1732 cm^{-1} was detected in smaller quantity in addition to nitryl fluoride.

After the evaporation of the volatile part, a solid white material was obtained (150 mg) which was stable up to room temperature. Quantitative analysis gave the following results: F = 34.6, 35.1%; Acidity, 28.85 meq/g.

Reaction between nitric acid and chlorinetrifluoride

Two ml. of red fuming nitric acid was added dropwise to 10 ml. of ClF_3 in a quartz trap at -78°C . A vigorous reaction took place and the reaction mixture was worked up similarly as described before. The volatile part was composed of, as identified by their IR spectra, SiF_4 , ClF_3 , ClO_2F , NO_2 , HNO_3 . A white solid residue was obtained. It melted at around -10°C . and reacted rapidly with the quartz container liberating SiF_4 . After the reaction, a liquid remained which was found to contain mostly nitric acid with some dissolved nitrogen oxides.

Complex formation between nitrosylfluoride and ClF_3

Ten ml. of chlorinetrifluoride was condensed into a two-necked flask at -78°C . and nitrosylfluoride was introduced in a slow stream. The precipitation of a white crystalline solid was observed. The excess chlorinetrifluoride was pumped off. The remaining white solid started to decompose at around 0°C .

Complex formation between nitrosylfluoride and ClF

Fifty ml. of CCl_3F was placed in a two-necked flask and it was saturated with ClF (b.p. = $101^\circ C$.) at $-78^\circ C$. Then nitrosylfluoride was passed into the solution at the same temperature and the precipitation of a white solid was observed. As the temperature was raised slightly, the solid started to decompose with a blue color.

Reaction of perchlorylfluoride with ClF

The reaction was carried out as described above, but instead of nitrosylfluoride, perchlorylfluoride (ClO_3F) was bubbled in. No solid formation was observed later when the temperature was increased gradually to $+20^\circ C$.

Miscellaneous

A few weeks were lost because of moving to another specially designed laboratory from our temporary place.

1s

August 25, 1964